

Low-temperature specific heat and thermal conductivity of glycerol

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We have measured the thermal conductivity of glassy glycerol between 1.5 K and 100 K, as well as the specific heat of both glassy and crystalline phases of glycerol between 0.5 K and 25 K. We discuss both low-temperature properties of this typical molecular glass in terms of the soft-potential model. Our finding of an excellent agreement between its predictions and experimental data for these two independent measurements constitutes a robust proof of the capabilities of the soft-potential model to account for the low-temperature properties of glasses in a wide temperature range.

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It is well established^{1,2} that glasses or amorphous solids exhibit thermal properties very different from those of crystalline solids and, even more strikingly, very similar among themselves irrespective of the type of material, chemical bonding, etc. At temperatures $T < 1$ K, the specific heat C_p of non-metallic glasses is significantly larger and the thermal conductivity κ orders of magnitude lower than those found in their crystalline counterparts. C_p depends approximately linearly ($C_p \propto T$) and κ almost quadratically ($\kappa \propto T^2$) on temperature, in contrast to the cubic dependences observed in crystals for both properties, well understood in terms of Debye's theory. At $T > 1$ K, C_p still deviates strongly from the expected $C_{\text{Debye}} \propto T^3$ dependence, exhibiting a hump in C_p/T^3 . In the same temperature range the thermal conductivity exhibits a universal *plateau*.

In 1972, Phillips³ and Anderson, Halperin and Varma⁴ introduced independently the well-known tunneling model (TM), whose fundamental postulate was the ubiquitous existence of small groups of atoms in amorphous solids which can tunnel between two configurations of very similar energy. This simple model of two-level systems or tunneling states successfully explained the low-temperature properties of amorphous solids⁵, though only for $T < 1$ K. On the contrary, the also rich universal behavior of glasses above 1 K (the hump in C_p/T^3 and the plateau in the thermal conductivity, or the remarkable feature in the vibrational density of states $g(\nu)/\nu^2$ at low frequencies known as the *boson peak*) still remains a matter of debate. One of the best accepted approaches to understand all the general behavior of glasses in the whole range of low-energy excitations is the phenomenological soft-potential model (SPM), which can be regarded as an extension of the TM. The SPM^{6,7} postulates the coexistence of extended lattice vibrations (sound waves) with quasilo-calized low-frequency (*soft*) modes. In this model, the potential of these soft modes has a uniform stabilizing fourth-order term W . In addition, each mode has its individual first-order asymmetry D_1 and second-order restoring force terms D_2 , which can be either positive or negative. Similarly to the TM, a random distribution

of potentials is assumed: $P(D_1, D_2) = P_s$. The SPM has been developed^{6,7,8,9,10,11} and reviewed^{12,13} in earlier papers where the interested reader is referred to.

Glycerol [$\text{C}_3\text{H}_5(\text{OH})_3$] is probably the most widely studied¹⁴ glass-forming liquid. Its high viscosity at a melting point around room temperature ($T_m = 291$ K) provides experimentalists with a very convenient temperature range where the supercooled liquid can be studied. Below the glass transition at $T_g \simeq 185$ K, the frozen-in liquid becomes a glass with a relatively weak, hydrogen-bonded network structure. Despite its good glass-forming ability, glycerol can also be obtained in an orthorhombic crystalline state¹⁵, with four $\text{C}_3\text{H}_5(\text{OH})_3$ molecules per unit cell, building up a structure of infinite hydrogen-bonded chains¹⁶. Several measurements of the specific heat of this well-known glass have been indeed reported^{17,18,19,20}, though not reaching temperatures below 1.5 K in any case. A broad maximum in C_p/T^3 was clearly observed^{19,20} around 8.5 K, but the expected existence of tunneling states could not be determined, since it requires temperatures typically below 1 K. Furthermore, Calemczuk *et al.*²⁰ also measured the specific heat of the crystalline state of glycerol, but only down to 5 K, hence not reaching temperatures low enough as to assess its Debye coefficient. On the other hand, there are no published thermal-conductivity data at low temperatures neither for glycerol nor for any other similar molecular glass. This is very probably due to the experimental difficulties of adapting the thermal-conductivity technique to a sample which is liquid at ambient temperature and must be thermally controlled *in situ* to freeze it into the glass state, maintaining at the same time an appropriate geometry and a moderate heat flow for the thermal conductivity to be correctly measured. To our knowledge, only a few orientationally-disordered ("glassy") *crystals* from other molecular liquids have been measured^{21,22}.

In this work, we report thermal-conductivity data of glassy glycerol measured from 1.5 K to around 100 K, as well as specific-heat measurements of both glassy and crystalline glycerol between 0.5 K and 25 K. In addition, we make concurrent use of both thermal properties measured for the glassy state in order to test the validity of

the soft-potential model in a typical molecular glass.

In Fig. 1(a), we show our thermal-conductivity data of glassy glycerol obtained by cooling *in situ* below T_g at a rate around -1 K/min liquid glycerol (Merck, anhydrous, used without further purification), placed inside a very thin-walled (0.2 mm) nylon tube. Standard steady-state techniques were employed. The thermal conductivity of the empty nylon tube was independently measured and subtracted. As can be seen, glycerol exhibits the thermal-conductivity behavior typical of glasses, with a plateau around 10 K quantitatively very similar to that of strong, network glasses as As_2S_3 and GeO_2 , i.e., a relatively high thermal conductivity among glasses. Therefore, glycerol could be a useful heat exchange medium at low temperatures when used as a glassy matrix.

Let us first analyze the thermal conductivity of glycerol within the soft-potential model. According to the SPM⁸, the inverse mean-free path of the phonons carrying out the heat is simply the sum of three contributions: the resonant scattering of the sound waves by either tunneling states or by *soft* vibrational modes, and the scattering by classical relaxational processes in the same asymmetric double-well potentials responsible of the tunneling states. From these premises, and inserting the corresponding SPM expressions for these three inverse mean-free paths, the thermal conductivity κ was found to be^{11,13}

$$\kappa = \frac{2k_B}{3\pi\bar{C}} \left(\frac{W}{h} \right)^2 F(z), \quad (1)$$

where

$$F(z) = \int_0^\infty dx \frac{x^3 e^{-x}}{(1 - e^{-x})^2} \frac{z^2}{1.1 \tanh(x/2) + 0.7z^{3/4} + x^3 z^3 / 8} \quad (2)$$

\bar{C} is the usual (averaged over longitudinal and transverse acoustic modes) dimensionless constant of the TM, directly related to the universal plateau in the internal friction $Q^{-1} = (\pi/2)C$, and $z = k_B T / W$, where the energy W is the aforementioned parameter of the SPM, which marks the crossover from the tunneling-states region at the lowest temperatures to the soft-modes region above it. Indeed, W can be determined^{11,13} from the position of the maximum T_{max} in a κ/T versus T plot:

$$W \simeq 1.6 k_B T_{max}. \quad (3)$$

T_{max} therefore separates the low-temperature range where resonant scattering by tunneling states dominates ($\kappa \propto T^2$) from higher temperatures ($\kappa \approx \text{const}$) where the soft modes are the main scatterers of acoustic phonons.

Fig. 1 shows that SPM eqs. (1-2) provide a good fit to thermal-conductivity data of glycerol from the lowest temperatures up to the end of the plateau around 30 K. The two parameters, W and \bar{C} are easily obtained^{11,13} from the κ/T plot [Fig. 1(b)]: the maximum position gives $W = 4.3$ K and its height $\bar{C} = 1.9 \times 10^{-4}$. The latter

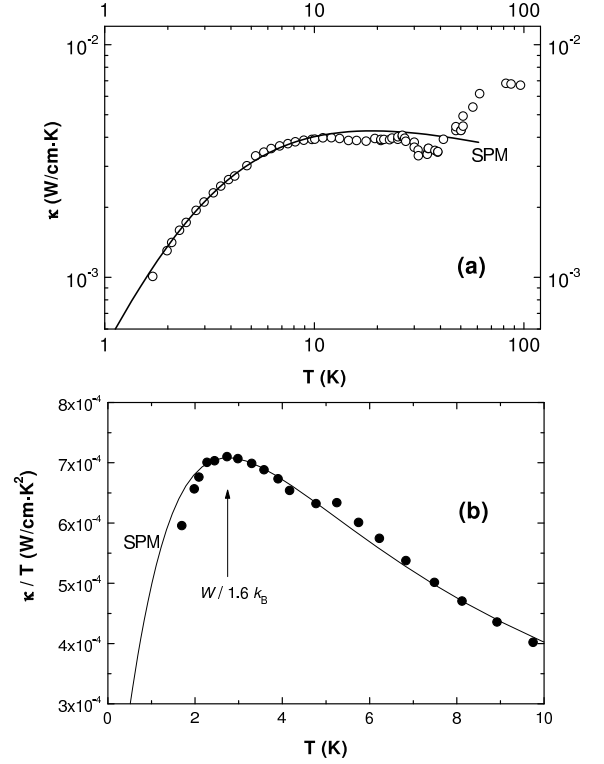


FIG. 1: Low-temperature thermal conductivity of glassy glycerol. (a): Thermal conductivity as a function of temperature in a log-log plot. Solid line is a fit to the soft-potential model (SPM). (b): Thermal conductivity divided by temperature below 10 K. The maximum marks the crossover from tunneling states to quasilocalized vibrations (soft modes) as dominant scattering centers for the “phonons” and allows a direct determination of the SPM parameter W .

constitutes indeed a prediction for the low-temperature internal friction of glycerol, never measured to our knowledge: its plateau value should be around $Q^{-1} \approx 3 \times 10^{-4}$, up to^{11,13} $1.2W/k_B \simeq 5$ K, where the rise due to thermal relaxation should occur.

Our specific-heat measurements of glassy and crystalline states of glycerol are presented in Fig. 2 (in a log-log plot showing the whole low-temperature range) and in Fig. 3 (in a C_p/T vs T^2 plot at the lowest temperatures to address the tunneling-states range for the glass and the Debye limit for the crystal). The heat capacity was measured in a ^3He -cryostat, employing a low-temperature quasi-adiabatic calorimetric cell, similar to one previously used in a ^4He -cryostat^{23,24}. The liquid glycerol is placed in a vacuum-tight, thin-walled copper can, with a fine mesh of copper fitted inside to facilitate thermal equilibrium. A thin gold wire was used as heat switch to cool the experimental cell. The subtracted addenda contribution to the total measured heat capacity at 4.2 K (1 K) was about 15 % (22 %) for the glass and about 30 % (50 %) for the crystal. The glass state was obtained by simply cooling the liquid from room temperature down to liquid-helium temperatures. After having

measured its heat capacity at low temperature, glassy glycerol was slowly heated above T_g (calorimetrically observed to take place at 185 K) until it crystallized around 250–260 K. Once this first-order, exothermic transition was completed, the sample was cooled again and the heat capacity of the crystal measured.

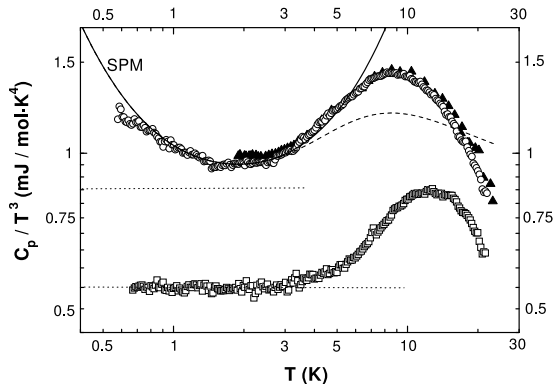


FIG. 2: Low-temperature specific heat C_p/T^3 of glass (\circ) and crystal (\square) phases of glycerol for the whole measured temperature range in a log-log scale. Solid triangles are published data from Leadbetter and Wytherley¹⁹. Dotted lines show the correspondent Debye contributions to the specific heat either measured calorimetrically (crystal) or estimated from sound velocities (glass). Solid line shows the curve calculated with the soft-potential model (SPM), taking the parameter W from the thermal conductivity data. Dashed line shows the same SPM calculation, but with a gaussian cutoff of the asymmetry for soft modes at high energies (see text).

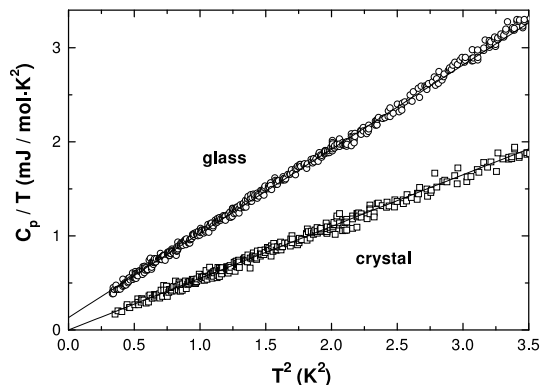


FIG. 3: Low-temperature specific heat of glass and crystal phases of glycerol in a C_p/T vs T^2 plot. Symbols are as in Fig. 2. Solid lines are least-squares linear fits.

In Fig. 2, published data for the glass between 1.9 and 25 K from Leadbetter and Wytherley¹⁹ can be seen to show a very good agreement with our data. There is also a good agreement with data for the crystal above 5 K²⁰. The low-temperature cubic Debye contributions are also indicated in that figure: for the crystal, it has been obtained from a least-squares linear fit below 1.5 K in Fig. 3, giving a Debye temperature $\Theta_D = 367$ K; for the glass, it can be estimated from zero-temperature extrapolations

of elastic data^{25,26,27} to be $\Theta_D = 317$ K. In contrast to the crystal, where C_p holds the expected Debye behavior for $T \leq \Theta_D/50$, the glass exhibits the typical excess over the Debye contribution in the whole low-temperature range. Within the SPM, these additional excitations are understood as soft quasiharmonic vibrations in single-well potentials responsible for the “boson peak” in C_p/T^3 , together with tunneling states arising from related double-well potentials responsible for the quasilinear contribution. The latter dominates below the minimum T_{\min} in C_p/T^3 given by $W \approx 1.8 - 2k_B T_{\min}$ ^{12,13}, and is more clearly observed in Fig. 3, where a linear coefficient $\gamma = 0.13$ mJ/mol·K² can be obtained (i.e., $\gamma = 1.4$ μ J/g·K² that is very similar to those values found in typical network glasses^{1,2,5}).

Finally, we wish to compare the specific-heat data of glassy glycerol with the behavior predicted by the SPM, once we have previously obtained its basic parameter $W = 4.3$ K from thermal-conductivity data. As said above, the SPM postulates the coexistence of extended sound waves with quasilocalized modes, either tunneling states in double-well potentials or quasiharmonic vibrations in single-well potentials, with a gradual crossover between them characterized by the energy W . Therefore, we can write the specific heat for a glass as

$$C_p = C_{\text{Debye}} + C_{\text{TLS}} + C_{\text{sm}}, \quad (4)$$

where C_{sm} is the contribution of soft modes (see below), and the contribution of the tunneling states C_{TLS} is determined, as in the TM, by means of the well-known expression for two-level systems⁵, using the correspondent density of tunneling states in terms of the SPM (eq. (4.7) in Ref.¹² or eq. (9.30) in Ref.¹³).

In the standard SPM, the density of quasiharmonic soft vibrations increases continuously with frequency as

$$g_{\text{sm}}(h\nu) = \frac{1}{8} \frac{P_s}{W} \left(\frac{h\nu}{W} \right)^4, \quad (5)$$

where P_s is the distribution constant of soft potentials. In the harmonic approximation, this leads to a specific-heat contribution from soft modes given by¹³

$$C_{\text{sm}} = \frac{2\pi^6}{21} P_s k_B \left(\frac{k_B T}{W} \right)^5. \quad (6)$$

The solid line in Fig. 2 shows the result of eq. (4), where $W = 4.3$ K was taken from the thermal-conductivity measurement and $P_s = 1.6 \times 10^{19}$ mol⁻¹ was simply determined to scale with experimental data.

Obviously, the *real* distribution of soft modes cannot grow with frequency $g_{\text{sm}}(\nu) \propto \nu^4$ unlimitedly. Gil *et al.*⁹ proposed a gaussian distribution in the asymmetry of the soft potentials (hence multiplying eq. (5) by an integral factor, see eq. (9.40) in Ref.¹³) based in a thermal strain *ansatz*, which without any further fitting parameter allowed them to account for the specific heat, thermal conductivity and vibrational density of states $g(\nu)/\nu^2$ in the

whole relevant range, including the “boson peak”. Alternatively, Gurevich *et al.*¹⁰ argued that the simple picture of independent quasilocalized harmonic vibrations coexisting with sound waves should fail at the Ioffe-Regel limit, not far above the boson peak. The interaction between soft modes would lead to a reconstruction of the vibrational density of states at higher frequencies, where delocalized soft vibrations with $g_{\text{sm}}(\nu) \propto \nu$ should dominate, therefore also explaining the boson-peak feature. Furthermore, hybridization of acoustic phonons with quasilocalized modes has been proposed to set in around the boson peak²⁸. For the sake of completeness, we also show in Fig. 2 by a dashed line the result of the total SPM prediction for the specific heat if the above-mentioned correction^{9,13} of eq. (6) is used. As can be seen, the position of the maximum in C_p/T^3 (which only depends on W and the glass transition temperature T_g , hence being determined without any free parameter) is very well predicted, though its height is not so well accounted for. However, these quantitative agreements or disagreements of the SPM around or above the boson peak are perhaps not very relevant, since the low-energy limits of both independent quasilocalized modes and Debye acoustic phonons (note that even in the crystal, C_p starts to deviate from the cubic limit above 5 K) should begin to fail there, for the reasons mentioned above. Nevertheless, one may conclude that the maximum in C_p/T^3 of glasses (i.e., the boson peak) is just the fingerprint of the end for the low-energy distribution of independent

soft modes, which govern low-temperature properties and low-frequency dynamics of glasses.

In any case, it is noteworthy that with only a constant factor P_s , used as free parameter to fit the height of the $C_p(T)$ curve (W was independently determined from thermal-conductivity data), the SPM is able to account consistently for the specific heat of this glass in the low-temperature range, from the tunneling-states region below 1 K up to the broad peak in C_p/T^3 , including the crossover region around the minimum in C_p/T^3 .

In summary, we have concurrently measured two low-temperature thermal properties of a paradigmatic molecular glass, glycerol, as well as the specific heat of the crystalline phase between 0.5 K and 25 K, hence being able to determine its Debye temperature. At lower temperatures, both properties for the glass exhibit a typical behavior indicative of the existence of tunneling states. Moreover, we have used these data as a new test of the SPM, which has been shown to successfully explain the specific heat and the thermal conductivity in a wide temperature range, also for a molecular glass such as glycerol.

Acknowledgments

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